

Development and Deployment of In-Situ Mass Spectrometers

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LONG-TERM GOALS

Long-term goals for this project include deployment of mass spectrometers on network class autonomous underwater vehicles (AUVs) for *in-situ* detection, quantification and mapping of both volatile and non-volatile species in the water column. Ultimately we envision adaptation of our instruments as self-directed, true panoramic chemical sensors capable of, e.g., tracing dispersion of chemicals from point sources and investigating the evolution of reactive chemical species.

OBJECTIVES

The objectives for this proposal period were diverse, including a wide variety of underwater mass spectrometer (MS) deployments, improvements of the existing underwater systems, and evaluation and development of alternative sampling interfaces and mass spectrometers. Proposed deployments included pollution monitoring at various sites in both freshwater and seawater, investigations of hydrothermal vents, and continuation of efforts to develop the technology and logistics required to create chemical maps of bodies of water. Instrumental developments were to include upgrades in the communication systems of the underwater mass spectrometers, continued construction and testing of a sampling interface for semi-volatile compounds, and evaluation of a portable laser desorption/ionization mass spectrometer for in-situ detection of non-volatile species in water.

APPROACH

Our approach to underwater mass spectrometry development has been modular and stepwise, initially involving simpler designs, while simultaneously testing other subsystems for more ambitious configurations. A long-term goal is to combine atmospheric pressure ionization, referred to as electrospray ionization (ESI), with mass spectrometry and tandem mass spectrometry (MS/MS) using

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| 14. ABSTRACT Long-term goals for this project include deployment of mass spectrometers on network class autonomous underwater vehicles (AUVs) for in-situ detection, quantification and mapping of both volatile and non-volatile species in the water column. Ultimately we envision adaptation of our instruments as self-directed, true panoramic chemical sensors capable of, e.g., tracing dispersion of chemicals from point sources and investigating the evolution of reactive chemical species. | | | | | |
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an ion trap mass spectrometer. Sample pretreatment and analyte separation using microfluidic devices will be performed prior to electrospray ionization when necessary. This system will allow detection and identification of non-volatile compounds at trace levels, with a very high degree of certainty, in complex marine environments. In a multifaceted approach toward this goal, we are evaluating a variety of types of mass spectrometers with unique capabilities. We are also testing and using simpler sampling methods, such as membrane introduction of volatile organic species. Our approach includes miniaturization of components, wherever possible, by incorporation of micro-systems technology (MST) and use of micro-electromechanical systems (MEMS).

WORK COMPLETED

The major instrumental developments during this funding cycle consisted of refinements and upgrades to the 200-amu linear quadrupole system to improve both performance and ease of use, and continued construction and testing of an automated solid phase microextraction prototype system for detection of a wide variety of polar and non-polar species in water. The plan to acquire and test a portable laser desorption/ionization mass spectrometer was postponed due to a change in the funding situation at the Johns Hopkins University Applied Physics Laboratory (the organization that was to provide the system to USF). As a result, a request was submitted and approved to reallocate the budgeted funds for the laser MS system, to support another set of deployments at Yellowstone National Park.

200-amu Linear Quadrupole Mass Spectrometer

The deep-water sampling pump and membrane interface, installed in the 200-amu linear quadrupole system last proposal period, were both refined to increase sensitivity and reliability for deployments to 200 meters depth. In addition, a 200-meter tether was obtained that allows access to shipboard power, and remote communication with the underwater mass spectrometer at these depths.

Automated Solid Phase Microextraction

During the last proposal period, we began to develop an automated solid phase microextraction (SPME) system that should be ideal for detecting a wide variety of polar and non-polar compounds (the current membrane interface provides very sensitive detection limits for non-polar volatile compounds, but does not transmit polar species with high efficiency). This effort has continued into this funding cycle. A prototype SPME interface has been constructed and interfaced with a laboratory ion trap mass spectrometer. Detection of polar compounds such as caffeine has been demonstrated. Components for the portable underwater version have been purchased and are presently being assembled for laboratory testing.

RESULTS

Chemical Mapping (200-amu Linear Quadrupole)

We have continued deployments of the underwater mass spectrometer on manned and unmanned, vehicles. In conjunction with these deployments we simultaneously obtain global positioning system (GPS) data to coordinate locations and analytical results (chemical concentrations). We are able to track and plot the vehicle/mass spectrometer path in real-time. Chemical maps are created after the deployment. An example of this chemical mapping capability is shown in Figure 1. The 200-amu underwater mass spectrometer was mounted just below the water surface on the ENG Concepts Guided

Surface Vehicle (GSV-2) and was remotely driven across Lake Maggiore in St. Petersburg, FL. Multiple dissolved gases were monitored at a cycle rate of approximately 1 Hz. Figures 1a and 1b show the relative concentrations of oxygen (m/z 32) and carbon dioxide (m/z 44). These concentrations varied inversely over most of the deployment route, indicating the presence of biologically driven processes (photosynthesis/respiration) in the lake. Significant changes in concentrations over very short distances demonstrate the need for a high spatial density of sampling. Such distributions are not observable using conventional collection techniques followed by laboratory analysis. The ability to monitor multiple gases simultaneously with one instrument should prove to be highly advantageous relative to use of typical in-situ sensors that target a single species.

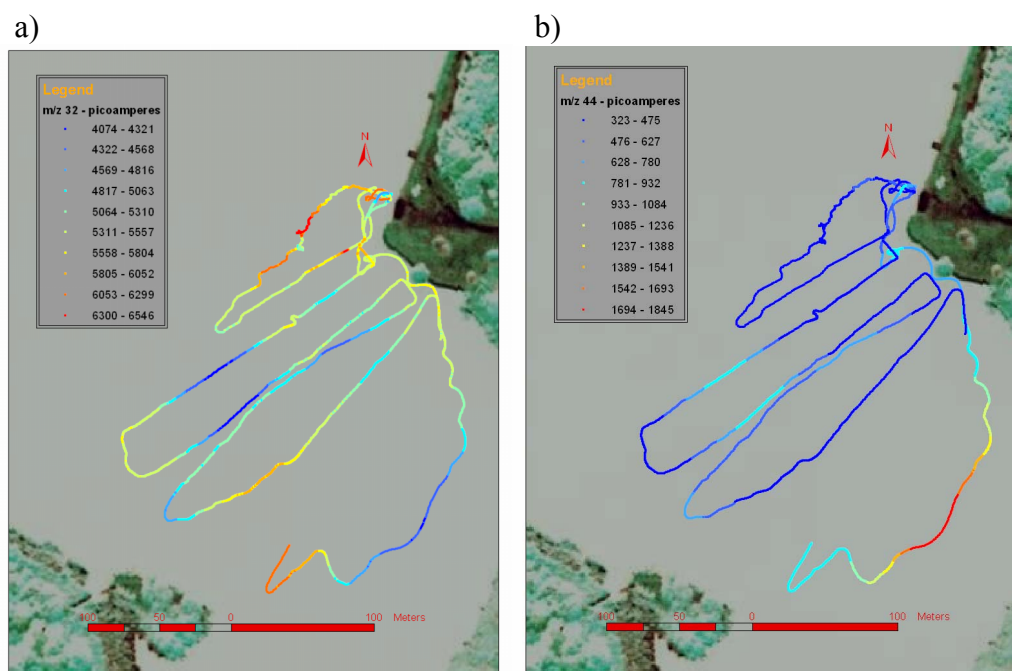


Figure 1. Maps of the intensity of a) m/z 32 (oxygen) and b) m/z 44 (carbon dioxide) during deployment of the 200-amu underwater mass spectrometer on a guided surface vehicle in Lake Maggiore, St. Petersburg, FL.

Kennedy Space Center (JESI) Deployments

The 200-amu underwater mass spectrometer was deployed in the lagoons and estuaries near Launch Pad 39A at the Kennedy Space Center (KSC) during August 2003. The deployments were part a multi-agency project titled the Joint Environmental Science Investigations (JESI) and was coordinated and partially sponsored by the National Undersea Warfare Center (NUWC). The purpose of these investigations was to enhance knowledge of fishery dynamics at key aquatic habitats on the Merritt Island National Wildlife Refuge, and demonstrate an effective collaboration of multiple Federal and State agencies in performing cooperative research. Both stationary-monitoring and transect-type mass spectral data were collected over a 5-day period. These data are presently being processed. The transect data were collected using a mobile sensor platform, MARVIN, provided by the Florida Marine Research Institute.

Yellowstone Lake Vent Analysis

We have very recently (2nd half of September 2003) used the 200-amu underwater mass spectrometer on a remotely operated vehicle (ROV) for continued studies of hydrothermal vents in Lake Yellowstone (Yellowstone National Park). As in the last proposal period, we integrated our underwater MS with the Eastern Oceanics ROV, supplied by Dave Lovalvo. This work was performed in collaboration with a University of Wisconsin, Milwaukee (UWM) group led by Val Klump. The UWM group supplied a water sampling system as well as in-situ sensors to complement the mass spectral data. In addition to studying the gas composition of the lake's deep hydrothermal vents, we sampled surface water collected while the R/V Cutthroat was in transit. During these transects we were able to detect changes in carbon dioxide and methane in the surface waters above some vent sites. These data sets will be analyzed in the very near future.

IMPACT/APPLICATIONS

We believe that *in-situ* mass spectrometers will become the most powerful deployable chemical sensors in the marine environment. Due to the versatility of mass spectrometry and MS/MS for detection and quantification a wide variety of compounds in complex environments, underwater MS sensors should have extremely broad application in environmental, chemical, biological and marine science.

TRANSITIONS

An exclusive licensing agreement for the membrane introduction/quadrupole mass filter version of the *in-situ* mass spectrometer has been negotiated with Applied Microsystems, Ltd.

RELATED PROJECTS

Another ONR-funded project entitled "ASCIuP: Fieldable Microsystems" is an extension of the microfluidic work originally performed in this project. The ONR-funded project entitled "Development of an In-Situ Mass Spectrometer for Stable Isotope Analysis" is also an extension of this project.

PUBLICATIONS

"Applications of underwater mass spectrometers in the marine and freshwater environment", P.G. Wenner, F.H.W. van Amerom, J.E. Edkins, S.K. Toler, K. Koehn, R. J. Bell and R.T. Short, *Proceedings of the 51th ASMS Conference on Mass Spectrometry and Allied Topics*, Montreal, CA (2003).

"Underwater mass spectrometers to monitor coastal waters, harbors, bays, lakes and streams" Strawn K. Toler, David P. Fries, Peter G. Wenner and R. Timothy Short, *Proceedings of A Major Role for Mass Spectrometry in Homeland Security: Past, Present and Future*, Knoxville, TN (2003).

PATENTS

Utility Patent Applications, Serial no. 09/971,116 and 09/971,119 entitled "Portable Underwater Mass Spectrometer" are presently under review by the US Patent Office.